

# Soft X-ray emission spectroscopy of polycyclic aromatic hydrocarbons

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## Abstract

High-resolution CK X-ray emission spectra of polycyclic aromatic hydrocarbons (PAH) were measured using synchrotron radiation. The main peak energies in the PAH X-ray spectra shifted to a higher energy region as the ratio of hydrogenated outer carbon atoms to the non-hydrogenated inner carbon atoms increased. Discrete variational (DV)-X $\alpha$  molecular orbital calculations provided theoretical confirmation that the spectral features depend on the ratio of hydrogenated/non-hydrogenated carbon atoms, which suggests that the features around the main peaks provide the information of the degree of hydrogenation in PAH compounds.

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## 1. Introduction

Soft X-ray emission and absorption spectroscopy with highly brilliant synchrotron radiation recently has been utilized to characterize various carbon materials [1–6]. The technique reveals electronic structure information about both occupied and unoccupied orbitals, which directly reflect the local structure and chemical bonding states. High-resolution soft X-ray absorption spectroscopy provides especially useful characterizations from the observed fine structures on the spectra. These fine structures have rarely been measured by typical electron energy loss spectroscopy (EELS) [7,8], which generally has lower energy resolution than soft X-ray absorption spectroscopy using synchrotron radiation. On the other hand, in soft X-ray emission spectroscopy many carbon materials usually exhibit broader structures than in X-ray absorption spectra. Therefore, it is more difficult to extract fine information on the electronic structure/chemical bonding states of unknown carbon materials by X-ray emission spectroscopy than by X-ray absorption spectroscopy.

To extract useful information on the chemical bonding states of carbon materials from their soft X-ray emission spectra, we have measured CK X-ray emission spectra of

various polycyclic aromatic hydrocarbon (PAH) compounds using synchrotron radiation. We focused on PAH which can be regarded as components of important industrial carbon materials, such as carbon black and carbon nanotubes. In this paper we describe the CK X-ray emission spectra of various PAH compounds, and subtle differences in spectral features are discussed relative to their chemical bonding states.

## 2. Experiment

Commercially available PAH compounds (*p*-terphenyl, anthracene, naphthacene, pentacene, triphenylene, pyrene, perylene, coronene), and highly oriented pyrolytic graphite (HOPG) were used for the spectroscopic measurements. The molecular structure of the PAH compounds are described in Fig. 1. Powder samples of PAH were pressed and held on indium-sheet substrates prior to being mounted on sample holders in the vacuum experimental chambers. Spectroscopic measurements were performed at the advanced light source (ALS). Soft X-ray emission spectra in the CK region were measured using a grating X-ray spectrometer installed in the undulator beamline, BL-8.0.1 [9]. The photon energy of the monochromatized incident beam was tuned to about 320 eV to effectively excite the C 2p electrons while preventing multiple ionizations. The resolving power ( $E/\Delta E$ ) of the spectrometer was estimated to be approximately 750 in the

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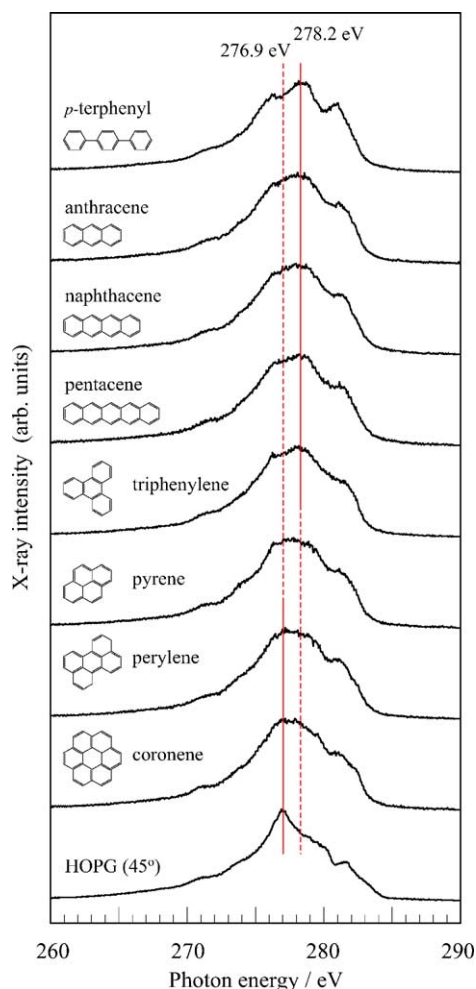


Fig. 1. Soft X-ray emission spectra in the CK region of polycyclic aromatic hydrocarbons (PAH) and highly oriented pyrolytic graphite (HOPG). Excitation energy is tuned to 320 eV.

CK region, using a 50  $\mu\text{m}$  entrance slit and a 600 lines/mm spherical grating with a 5 m radius. Both the angle of the excitation beams incident to the sample surface and the take-off angle of X-rays emitted from the surface were fixed at 45°. Measurement time for each sample, except for *p*-terphenyl, was set at 10 min, and sample decompositions were hardly observed during the measurements. For *p*-terphenyl, spectra were obtained by 10 times accumulation of 1 min measurements on every fresh sample position, because *p*-terphenyl is easily decomposed by undulator radiation.

### 3. Results and discussion

Fig. 1 shows the CK X-ray emission spectra of the PAH compounds and HOPG. In *p*-terphenyl, a three-peak structure is observed clearly; the three peaks are observed at 276.0, 278.2, and 282.0 eV. The three-peak structure of *p*-terphenyl is similar to the spectral features of benzene [10]. This suggests that the electronic structure of each ben-

zene ring in *p*-terphenyl is isolated by single C–C bonds and that the electrons in each benzene ring are fairly localized in the individual rings. No three-peak structure is observed in the condensed aromatic hydrocarbons. However, broad main peak features are observed around 278 eV and high-energy shoulders around 281 eV. This suggests that electrons in the condensed aromatic structures are delocalized over the molecules due to the  $\text{sp}^2$ -hybridization in all of these molecules, which results in spectral feature broadening. In the broad main peak features of the PAH compounds, however, the peak energy shift depends on the molecular structure. The main peak energies of anthracene, naphthalene, triphenylene, and 2,3-benzotriphenylene, seem to be 278.2 eV, which corresponds to the centered-peak energy in *p*-terphenyl. In pyrene, the peak seems to shift to a lower energy. In perylene and coronene, peak energies clearly were shifted to 276.9 eV. It should be mentioned that the shifted energy of 276.9 eV corresponds to the peak energy of HOPG which can be regarded as a large PAH compound.

As mentioned earlier, the main peak energy of 278.2 eV in anthracene is the same peak energy in both *p*-terphenyl and benzene, and the peak energy of 276.9 eV in coronene is the same peak energy found in HOPG. One of the possible explanations for this peak energy difference among PAH compounds will be the chemical bonding difference of the carbon atoms: one peak represents hydrogenated outer carbon atoms and the other non-hydrogenated inner carbon atoms because each carbon atom of benzene bonds to hydrogen atoms, but carbon atoms of HOPG are essentially free of bonds to hydrogen atoms.

To explain the peak energy shifts among PAH compounds, including HOPG, the electronic structure of coronene was analyzed by discrete variational (DV)-X $\alpha$  molecular orbital (MO) calculations as a typical demonstration [11,12]. Prior to the DV-X $\alpha$  MO calculations, the molecular structure of coronene was optimized by molecular mechanic (MM) methods using commercially available MM2 software, and the coordinate data of the optimized individual atoms were input to commercially available DV-X $\alpha$  software. Fig. 2 shows the molecular structure of coronene and occupied C 2s and C 2p density-of-state (DOS) spectra obtained by the DV-X $\alpha$  MO calculations. The DOS spectra were obtained by broadening the DOS with 0.5 eV wide Lorentzian functions. Because the total C 2p DOS spectrum approximately reproduced the main-peak and high-energy-shoulder structures of the measured X-ray emission spectrum, it was confirmed that the calculation nearly reliable for spectral analysis in this system. In coronene, there are three types of carbon atoms (denoted by I–III in the upper panel of Fig. 2); one (I) is the outer carbon atoms bound to hydrogen atoms and the others (II and III) are inner carbon atoms not bound to hydrogen. The DOS spectra of the hydrogenated C(I) atoms and of non-hydrogenated, C(II) and C(III), atoms are shown separately in the lower panel in the figure. Although the C 2p DOS spectra of both hydrogenated C(I) atoms and non-hydrogenated C(II) and C(III) atoms show broad

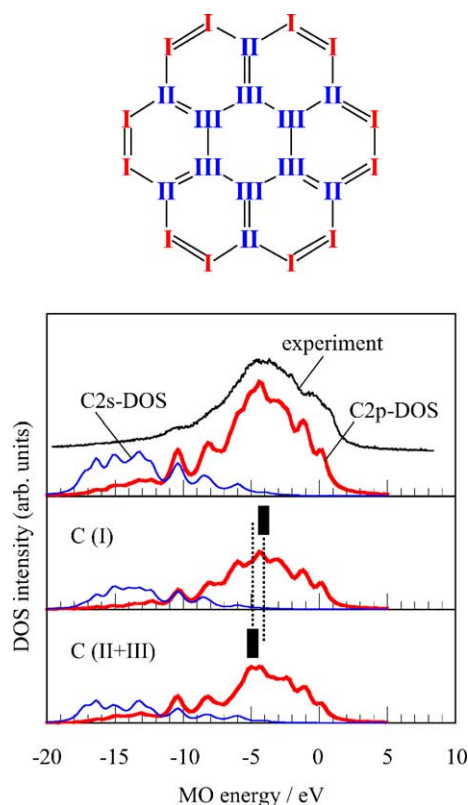


Fig. 2. Molecular structure (upper panel) of coronene and the occupied C 2s and C 2p density-of-state (DOS) spectra of coronene. The measured X-ray emission spectrum of coronene is described on the total DOS spectra (lower panel). DOS spectra of hydrogenated carbon atoms (I) and of non-hydrogenated atoms (II and III) are illustrated individually.

features ranging over 15 eV, the peak energy difference is observed between the carbon atoms. The hydrogenated carbon atoms exhibit a higher-energy peak position than the non-hydrogenated carbon atoms. This peak energy difference on the MO energy is about 1 eV. From this analogy, we can estimate that PAH compounds, which take a higher ratio of hydrogenated outer carbon atoms to non-hydrogenated inner atoms, exhibit higher main peak energy. This suggests that information on hydrogenated outer/non-hydrogenated inner carbon atoms in PAH compounds can be obtained from the main peak features in the X-ray emission spectra.

To obtain quantitative chemical bonding state information on PAH compounds from their X-ray emission spectra, the main peak features in the region between the 276.9 and 278.2 eV were approximated with linear functions. The approximated linear functions on individual PAH compounds and their slopes are described in the upper panel of Fig. 3. Anthracene, naphthacene, pentacene, and triphenylene display a positive slope, pyrene has approximately a zero slope, and perylene, coronene and HOPG have negative slopes. The slopes are plotted in the lower panel as a function of the percentage of hydrogenated outer carbons. The data of

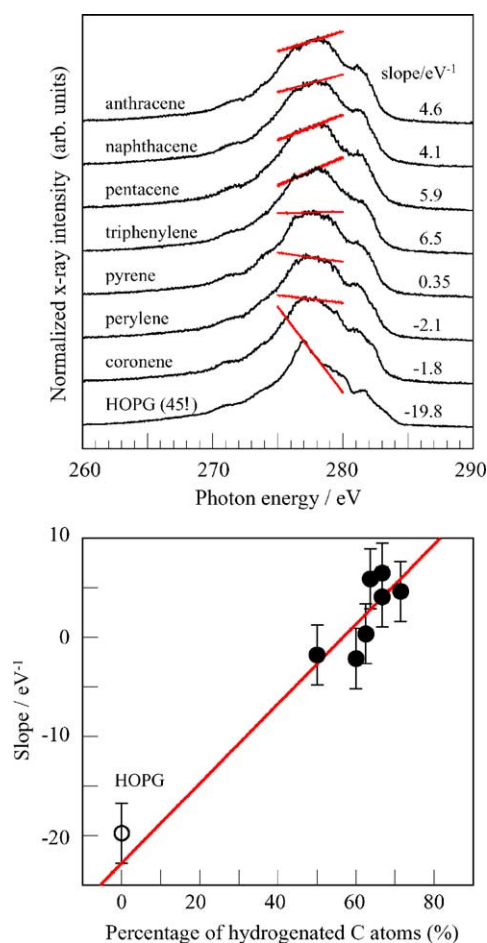


Fig. 3. The upper panel shows the approximated slopes near the main peaks of several PAH compounds. The lower panel shows the relation between the approximated slopes and the percentage of hydrogenated outer carbon atoms.

PAH compounds, except for HOPG, can be approximated by linear functions, represented in the figure by a solid line. In this figure, the percentage of hydrogenated carbon atoms in HOPG is assigned to be zero. Thus, the slope datum for HOPG is also on this approximated line to within the error bar. From this figure, it can be said that the linear relation between the slopes on the main peak features in the X-ray emission spectra of PAH and the percentage of hydrogenated outer carbon atoms can be expanded to HOPG. This finding means that we may easily extract the degree of hydrogenation in PAH materials.

#### 4. Conclusion

High-resolution, soft X-ray emission spectra in the CK region of PAH compounds were measured by synchrotron radiation. Spectral features at the main peaks depended on the molecular structures: peak energy shifts were observed in the region between 276.9 and 278.2 eV among the PAH

compounds. The energy at 276.9 eV corresponds to the main peak energy of HOPG and that of 278.2 eV to the main peak energy of benzene. Considering the relation between the main peak energy and hydrogenated/non-hydrogenated carbon atoms, we have plotted the dependence of the approximated slopes at the main peak features on the ratio of hydrogenated outer carbon atoms in individual PAH compounds. Thus, an approximately linear relation was observed between the slopes and the percentage of hydrogenated carbon atoms. The slope of the HOPG spectrum also agreed with this relation. This finding means that we may easily estimate both the degree of hydrogenation in PAH-based materials and the average component size of PAH structures from the X-ray emission spectra. This information is useful to characterize PAH-based materials, such as carbon black and carbon nanotubes.

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